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VAPOUR PHASE GROWTH OF THICK MONOCRYSTALLINE GaN EPITAXIAL LAYERS BY SANDWICH-METHOD.

3-d Interim Technical Report

by

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ABSTRACT

The characterization of the GaN epilayers from 70 to 250 μm thickness grown by SSM on the 6H-SiC substrates was performed. Free carrier concentration in initially undoped GaN samples was found to range between 2 and 6 x 10^{17} cm^{-3}. Rocking curve measurements of the GaN layers grown by SSM reveal the full width of half maximum (FWHM) from 150 to 400 arc.sec. Three-dimensional 15-20 arc.sec. disoriented wirtzite domains looked like the hexagonal prism in size of cells of 50 nm were found. Correlation between the spectral luminescence characteristics, its spatial inhomogeneity and structural perfection of the grown layers was shown. Increasing of wide-band emission in visual spectrum and it spatial inhomogeneity was suggested to be caused by the local stoichiometry deviation. The Fe, Ni, Mn impurities states in the GaN crystals were discovered and identified by the EPR method.

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REPORT

X-ray rocking curve measurements of the GaN layers of 70 to 250 μm thickness grown by SSM reveal the full width of half maximum (FWHM) from 150 to 400 arc.sec. Three-dimensional 15-20 arc.sec. disoriented wirtzite domains looked like the hexagonal prism of 200-300 nm length and the cell size of 50 nm were identified near the interface of SiC /GaN structure by the modified method of Small-Angle Scattering of X-rays (S-AS). Searching the nature of interfaces let us to state the fact that interface has crystalline nature of intermediate between GaN and SiC parameters.

Luminescence properties of GaN epilayers grown by sublimation sandwich-method on the SiC substrates have been studied. It was shown that the luminescence spectrum of initially undoped GaN epilayers depend on the crystal quality. A spectrum of the best samples demonstrates a powerful sharp line at 3.47 eV and 4 meV width caused bound exiton recombination was observed. The intensity of exiton line was 30 times more than the yellow band. The spatial inhomogeneity luminescence was studied both over the surface and cross-section by the method scanning electronic microscopy in the color cathodoluminescence mode (SEM-CCL). The separate bright spots or strips with a various radiation spectrum (from yellow up to blue) was observed. Blue luminescent band near the SiC/GaN interface was also found. Correlation between CL emission, luminescence inhomogeneity and morphological and structural defects of a grown layer was discussed. It is suggested, that local stoichiometric variation are responsible for inhomogeneity of luminescence.

We report on the observation of electron paramagnetic resonance of iron, manganese and nickel trace impurities in bulk GaN crystals grown by the sublimation sandwich method. The resolved hyperfine structure due to interaction with ^{55}Mn (I=5/2) nuclei has been observed in GaN, allowing unambiguous identification of the impurity. Manganese and nickel exist in Mn^{2+} ($3d^5$) and Ni^{3+} ($3d^7$) charge states with electron spin S=5/2 and S=3/2, respectively, and occupy gallium sites in the GaN lattice. For Mn^{2+} we found g=1.999, hyperfine structure

constant A=70·10^{-4}cm^{-1} and fine structure parameter $/D/$ = 240·10^{-4}cm^{-1}. The EPR spectrum of Ni^{3+} in GaN had the characteristic anisotropy of an S = 3/2 system in a strong axial crystalline field. The effective g-factor values were found to be $g_{||}{}' = 2.10$ and $g_{\perp}{}' \cong 4.20$ for a system with an effective spin $S' = 1/2$. An analogy was revealed between the parameters of Mn^{2+} and Ni^{3+} in GaN and ZnO crystals.

The optimization of growth system for providing great scope for control of GaN growth parameters was carried out. 20 epilayers on SiC substrates were grown.

2 papers and 4 reports have been submitted.

List of reports

1.E.N.Mokhov, A.D.Roenkov, G.V.Saparin, S.K. Obyden, P.V.Ivannikov and J.Freitas Characterization of GaN Epitaxial Layers by Color SEM-CL Method. Appl.Phys.Lett. 1997

2. Baranov P.G., Ilyn I.V., Mokhov E.N. Identification of iron transion group trace impurities in GaN bulk crystals by Electron paramagnetic resonance - Sol. St.Commun. 1997, v.101, N 8, p.611-615

3. M.E Boiko Studying Ddomains in Layers of GaN. International Conference on Silicon Carbide, III-nitrides and Related Materials-1997.ICSCIII-N'97 Sweden Aug. 31-Sept. 5, 97

4.. M.E. Boiko Incommensurate domains in gallium nitride plain slabs. The second International Conference on Low Dimensional Structures and International Conference on Advanced Materials'97 Lisbon, Portugal May 1997.

5.P.G.Baranov, I.V.Ilyin and E.N. Mokhov Identification of iron transition group in GaN bulk crystals by EPR Int.Conf. on Defects in Semicond. (ICDS-19), Aveivo, Porturgal,1997

6. M.E.Boiko, E.N. Mokhov, Yu.G. Shreter,. "Small-angle scattering of X-rays (S-AS) of GaN, deposited on SiC and Al_2O_3 substrates. E-MRS 97 Strasbourg ICAM`97 MRS-Strasbourg June 16-20, 1997

(2) Brief description of the research plans on staying period

1. Optimization of the growth conditions and thick GaN epilayers deposition on the large SiC substrates, grown by SSM.

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Analysis of electrical, optical and paramagnetic properties and spatial distribution of structural defects in GaN epilayers

1. X-ray characterization of structures quality

1.1. X-ray diffractometry

In our experiments we use standard (omega) - scan for characterization SiC substrates and GaN epilayers quality. In preparing X-ray installation (diffractometer URS-1.0 Burevestnik, Sanct-Petersburg) we changed standard crystal keeper in the monochromator device. We changed base distances from monochromator to crystal in study too. We choose Lely crystal SiC (0001) as crystal-monochromator. The full width at half maximum (FWHM) for this crystal is less than 13 arc.sec at (0006) rocking curve and 8 arc.sec at (000 12). High - accuracy adjustment of X-ray optics let us to get standard rocking curves for our characterization using $CuK\alpha_1$ radiation in combination with a plane SiC (0001) monochromator crystal.

The structural quality of GaN layers was studied by X-ray diffractometry (XRD) and Soller slits for the determination of peak width with high resolution. The angular resolution is approximately 3.6 arc.sec. which is smaller then the diffraction width of the peak observed from GaN.

The experiment utilized a 4-circle diffractometer which allowed the access to a large volume of reciprocal space. Several different types of scans were used to characterize the layers. Thus, if the film has the (0001) orientation, Θ-2Θ diffraction scans of these peak can determine the difference between the two polymorphs. The periodicities of the two structures are fundamentally different: a=3.186A, c=5.176A for wurtzite structure and a=4.530A, ($2d_{220}$=3.210A, $2d_{111}$=5.231A - for zinc-blende in wurtzite set).

We have found only the wurtzite phase and could not detect the zinc-blende GaN phase which often coexists in experiments of other authors. The presence of a coherent crystalline component in all of the grown layers was confirmed by well - defined, essentially Lorentzian x-ray diffractometer peaks (Figs.1.1; 1.2).

Double crystal X-ray diffraction (0002, 1 1 $\bar{2}$ 4) reflection profiles were recorded in parallel (**m-n**) setting with $CuK\alpha_1$ radiation.

In our experiments we studied more then 20 GaN/SiC structures. Some typical rocking curves are presented in Fig. 1.2; 1.3. For the most part the FWHM varied between 150 and 400 arc.sec. Rocking curve from one of the best samples is shown in Fig.1.2. Curves are the profile of a heterostucture of 70 μm GaN stacked 300 μm

SiC substrate illustrating the homogeneity present in epitaxial layers of this thickness. The layer reproduced the (0001) orientation (curve **a**) and its (1 1 $\bar{2}$ 4) direction (curve **b**) coincide with the (1 1 $\bar{2}$ 1) direction of the substrate. A sharp peak (0002) is resolved at ω=17.3 arc.deg. corresponding to the known equilibrium GaN lattice constant (2.589A). Other diffraction peaks of GaN polycrystalline structure were not observed. The intensities of SiC peaks are lower in comparison with GaN because of the adsorption in the GaN layer.

We have also performed measurements to examine the orientation of the grown layers. Rocking curves of ω, around the on-axis Bragg peaks were used to examine the orientation spread of the layer parallel to the surface normal (ω-scan). The spreading of **in**-plane orientations as well as the epitaxial relationship between substrate and layer axes **in** the plane were determined with φ-scans, in which the sample was rotated about its normal while ψ, 2Θ and ω were held fixed at the peak position.

The Fig.1.2. illustrates well the difference between the crystallographic quality of the bulk substrate SiC and the epitaxial GaN layer. Rocking curve measurements of the GaN layers reveal the full width of half maximum (FWHM) of 150 arc.sec. The FWHM for SiC substrate is 130 arc.sec. The broadening of the rocking curve for the layers is caused by mosaicity, strains and destruction of the x-ray wave coherence by extended defects (like dislocations). The obtained FWHM value is compared with the best FWHM of 100 arc.sec. reported by Nakamura [1] and Ferita [2] ($\Delta\omega$=40-100 arc.sec. for GaN layers thinner than 1 μm) grown by MOCVD. Nevertheless, the present data represent a significant improvement over the previous 1 μm layer reported by MBE [3].

1.2. Small-angle scattering characterization of GaN/SiC interface.

Structural characterization of gallium nitride properties, studying surfaces and interfaces were carried out by routine X-ray diffractometry (XRD) and by the modified method of Small-Angle Scattering of X-rays (S-AS). (S-AS) will be convenient if objective is the study of crystalline diffraction patterns of 50-200 nm.

We used for our X-rays measurements thick films (0.2-0.3mm) of the GaN deposited on (0001) plane of SiC substrate and thin (0.003-0.005mm) films GaN deposited on sapphire (α-Al_2O_3). X-ray rocking curves point out the difference in full width at half maximum (FWHM) of those structures. S-AS indicate difference in picture for those samples too.

We compare the shape data of ordinary X-ray diffractometry rocking curves of crystals with S-AS data. We propose the model of the domain wall grids for GaN deposited on SiC and Al_2O_3.

GaN films deposited on the SiC had the three-dimensional 15-20 arc.sec disoriented domains. GaN domains distribute in liquid cluster model. It is seen by presence of strong incident peak and weak size-of-cluster peak. Fig. 1.4. Upper view of the grid of GaN domains looked like the network of 120 or 60 degrees 50 nm cell.

Estimation the length (perpendicularly surface) of those rhombical-hexagonal prisms (columns) was 200-300nm. In other words it is column model of GaN crystal growth discussed in papers devoted to electron microscopy studying this process.

We determine the interface character GaN/SiC as the texture of the second order. We claim that the stresses in the film realize as domain walls.

The transmission mode S-AS carried out on GaN deposited on sapphire registers that variations of density are distributed by the gas-like model Figs.1.5; 1.6. It coincide with referring transmission electron microscopy (TEM) data. [4, 5]. The FWHM of X-ray rocking curves corresponding (000L) GaN reflection reveal a good quality GaN single crystalline film. As those films are 100 time thinner then SiC deposited, stresses can not crack across the film. We are to suppose that if the film would be thicker, the impurities can disorganize (cracks, domain walls formation) the film. The FWHM of such films are wider when film is thicker. We can connect these phenomena with less organizing role of interface GaN/Al_2O_3. It has no such regular nature as GaN/SiC interface has.

Searching the nature of interfaces let us to state the fact that GaN/SiC has very weak singlecrystalline rocking curve between GaN and SiC peaks. In GaN/ Al_2O_3 case signal level was low than noise level. It demonstrates that GaN/SiC interface has crystalline nature of intermediate GaN and SiC parameter. Similar picture corresponds to serching intermediate film of AlN in Ref.[7].

Structural characterization of GaN films grown under different growth conditions has also been carried out by number of workers. The major defects that have been reported in these films are dislocations, double positioning boundaries (DPBs), and inversion domain boundaries (IDBs). [7]

A typical low magnification image of a thick GaN epilayer grown on (0001) SiC, as viewed along an projection of the substrate has traces of interdomain boundaries. The GaN layer is epitaxial with respect to the substrate, also with an [0001] surface normal, and has-the wurtzite crystal structure. Transmission electron micrograph showing the GaN film extended defect structure (Fig2 from [4]).

It was observed that the wurtzite GaN was oriented epitaxially with the SiC substrate, i.e. the stacking direction of both crystals was parallel, and the domains were bounded by stacking faults. Such faults are commonly observed for materials which crystallize in more than one polytype. It appears that the partial dislocations associated with the stacking faults relieve the strain arising from the large lattice mismatch between GaN and the substrate, and allow the nucleation of the more

stable wurtzite GaN domains, which have lower bulk energy, rather than the metastable zincblende material.

There was found domain structure of GaN. In the first time we could to estimate average size of those domains. [6] If electron microscope data get local view of cross-section of such film, composite X-ray researches (XRD and S-AS) get average integral picture of the inner situation inside the film. With the accuracy of less 0.1% we can find GaN zincblende phase. Naturally, the volume of boundary planes vanish to zero, and we can not notice it.

1.3. Discussion.

Plain view of zincblende and wurtzite phase differs in crystal plane packing. In other words stacking fault is equivalence of thin monolayer intermediate zincblende phase between wurtzite domains. We can not to see it in direct way. We can not claim that it is zincblende phase as whole, only the possibility of the such construction is proposed basing on our X-ray and the electron microscope literature references. [5] We can to estimate shape and volume of average column - like domain. In TEM case they can estimate a random column shape of random cross section.

The GaN film contains a high density, of planar defects primarily originating at the substrate-epilayer interface. These defects are mostly stacking faults and microtwins that lie along the equivalent planes. However, the defect density decreases with increasing distance away from the interface. [7] Twins are often observed to terminate within the epilayer as a result of intersection with a second twin or by a process of mutual termination at a twin/matrix interface, as observed previously in heteroepitaxial growth of epilayers (Fig.3(a) from [7]).

Closer inspection of the interface reveals that it is uneven, and a high density of dislocations is also evident in the GaN epilayer, especially close to the interface. These defects could represent a mechanism for strain relief close to the substrate surface. The nucleation of stacking faults and microtwins originating at the interface. The lattice misfit between SiC and GaN is 3.4%, 8.4% in **a** and **c** direction respectively and, as a direct consequence of such mismatch, continuity of lattice planes across the interface could be expected.

In SiC materials, the (0001) surface is close-packed, having the lowest surface energy of the principal surfaces. Stacking faults and microtwins on the (0001) planes are common growth defects and could provide an other mechanism for accommodation of the lattice mismatch at the substrate surface.

A low magnification image of wurtzite GaN deposited directly on (0001) 6H SiC as a substrate the epilayer can be characterized in terms of columnar grain growth and extensive stacking defects running parallel to the film/substrate interface.

Close to the interface, the stacking sequence could be characterized as ..ABABAB.. corresponding to the hexagonal wurtzite stacking, but further away from the interface the stacking became almost random. The stacking faults are also evident from the streaking perpendicular to (0002).

In further efforts to obtain higher quality wurtzite GaN buffer layers were initially deposited on the (0001) 6H SiC substrate. The subsequent GaN deposited layer was effectively free of (0002) stacking defects and the-stacking sequence was ..ABABAB.. across the entire width of the film.

Columnar grains in the GaN layer, due here to slight differences in growth conditions, project into the GaN film thus lending a polycrystalline nature to the latter but without any amorphous regions. The GaN buffer layer is obviously heavily faulted with many planar defects, whereas the GaN epilayer has comparatively few defects as compared with the buffer (See Fig.3(a) [4]).

This phenomenon coincide with our data of random gas-like distribution GaN domains grown on Al_2O_3 substrate and liquid cluster model of GaN domains deposited on SiC. In our earlier studies of GaN/SiC, [6] it had been found that the defect density in GaN layers was reduced for thicknesses in excess of 100 nm.

1.4.Conclusion

Rocking curve measurements of the GaN layers grown by SSM reveal the full width of half maximum (FWHM) from 150 to 400 arc.sec. The obtained FWHM values are compared with the FWHM of epitaxial layers grown by other known methods. Three-dimensional 15-20 arc.sec. disoriented wirtzite domains looked like the hexagonal prism (column) of 200-300 nm length and the cells size of 50 nm were identified near the interface of SiC /GaN structure by the modified method of Small-Angle Scattering of X-rays (S-AS). Searching the nature of interfaces let us to state the fact that intreface has crystalline nature of intermediate between GaN and SiC parameters.

Only wurtzite domains were observed in the GaN samples investigated. Here, the formation energies of wurtzite and zincblende phases of GaN are assumed to be roughly equal. Hence, lowering the energy of the heteroepitaxial system by nucleating defects, does not create favorable conditions for nucleating the wurtzite phase, which is thermodynamically more stable. Nevertheless, because of large thermal (25% and 49%) and lattice (3.4% and 8.4%) mismatches[8], SiC is still not the ideal substrate material for wurtzite GaN heteroepitaxy.

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2. Electrical and optical properties and spatial distribution of structural defects

2.1.Introduction

The luminescence analysis is shown to be a powerful tool for control of crystal quality of the grown GaN epilayers. Sharp, narrow peak, at 3.47 eV corresponding to bound exiton recombination [1] is observed in high quality initial undoped GaN layers [2,3]. It can be assumed the degradation of crystallographic epilayer performance leads to the widening of above peak and wide-band emission appearance into view interval of the CL-spectrum caused by the deep emission centers.

This additional emission is considered to be to a donor-acceptor pair recombination which may originate from the deep levels caused by impurities and native defects which are introduced in the epilayer. It is known[1], for example, that acceptor impurities as Mg, Zn and Cd cause the bands appearance in visual interval of wave lengths dominantly in blue and violet parts of CL spectrum. Intensive yellow luminescence is very frequently observed in GaN-epilayers and some attempts were made to attribute this emission to the deep centers of unknown nature [4]. Earlier this emission was assigned to carbon [1].

Currently some serious evidence has been advanced that the center of yellow luminescence is an association including nitrogen vacancy [5,6]. The capability of several recombination mechanisms with participation of intrinsic defects and impurity is due to the dependence of GaN-epilayer luminescence vs the growth temperature, III/V molar ratio [3,7,8] and substrate orientation [9]. The band-edge luminescence peak intensity of the GaN epilayer, grown on the oriented exactly (0001) plane is below considerably, than epilayer grown on misoriented plane [9]. Authors believe that slight misorientation decreases the interioration of deep

impurities (Si, 0 and C, for example) and /or reduces the density of nitrogen vacancy.

The modification of the luminescence spectra is resulted from residual strain fields caused by the growth conditions [3]. This idea is confirmed by data published by Weeks et al [10], which demonstrates that there is tendency to shift of the luminescence spectrum to lower energies with decreasing GaN epilayer thickness. The assumption that value of residual strains is maximum near substrate-epilayer junction is valid. Really homoepitaxial layers of GaN have strong sharp exiton line and weak yellow band [11]. But these predictions require of further experimental confirmation.

Unfortunately, it is difficult to find an information in articles relative to the space luminescence inhomogeneity of grown layer. There is no question the luminescence inhomogeneities over the surface as well as epilayer thickness can essential to distort taken results. Obviously degradation of structure and morphologic epilayer performance leads to irregular luminescence. This conclusion is confirmed by followed experimental data. It was shown by Haramatu et al.[12] that inhomogeneous luminescence is measured when the surface growth process is carried out in a stepwise manner on vicinal plane. Next authors [13] also demonstrated that the microstructural defects (aggregates of dislocations) cause the CL inhomogeneity in the epitaxial GaN grown by MOCVD due to non-radiative recombination.

Currently the inhomogeneity luminescence of the GaN epilayers grown by sublimation sandwich method on the SiC and sapphire substrates have been studied. It was shown that structural and morphological defects cause the CL- spectral inhomogeneity of GaN-epilayers.

2.2. Experimental

The initial undoped GaN epilayer were grown by sublimation sandwich method on silicon carbide substrates in a horizontal quartz reactor with h.f. heating. The growth cell consists of a vapor source and a 6H- SiC single crystal substrate. The SiC substrates were oriented in the [0001]Si direction. The source material (Ga metal or GaN powder) is placed parallel to the substrate crystal with a small gap. The substrates of 6H SiC wafers grown by Lely method or sublimation sandwich method very used. High purity ammonia can be introduced into the growth cell to prevent GaN decomposition. Growth conditions close to equilibrium can be created for a wide temperature range, from 1000 to 1300°C for GaN. Such a system may be quasi-closed for its vapors adding to congruent transfer of the sublimated material from the source to the seed. As a result, we can grow bulk crystals and thick epilayers (about 0.1-0.5 mm thickness) at a rate of 0.2 to 1 mm/h. The effective

volume of the growth cell can be considerably reduced to obtain low levels of residual impurities and a high probability of utilizing all evaporated material, when its transport in the cell is close to 100%..

The GaN epitaxial layers were characterized by photoluminescence in the spectral range from 3.5 to 0.5 eV using a high-resolution grating monochromator or a Fourier transform spectrometer. The samples were excited with the 325 nm line of a HeCd laser. In the detector system a photomultiplier or liquid -nitrogen cooled Ge or InGaAs diode was used. Reflection and absorption measurements an the mid- and near-infrared at room temperature and 2 K were also performed on the Fourier transform spectrometer.

The color cathodoluminescence (CL) scanning electron microscopy (CCL-SEM) technique [14] was used for the study of the GaN epilayers deposited on the sapphire and silicon carbide substrates. The microscope was equipped with light detectors and a new backscattered electron detector. This technique using mixed true color contrast and black and white contrast recognizes local luminescence properties of materials, defects, specific inhomogeneities, and morphological peculiarities. Such capabilities allow to discovery of new information concerning growth structure of epitaxial GaN layers.

2.3. Results and discussion

We studied 25 GaN specimens grown by the above technique. The GaN layers showed **n**-type conductivity. Free carrier concentration determined by Hall-effect and optical absorption in the near -infrared range (1-2 μm) was found to range between 2 and 6 x10 ^{17} cm^{-3}. Electron mobility varied from 30 to 80 cm^2/V s.

Preliminary we measured luminescence properties of these samples. First samples group had intensive light blue luminescence peaked at 2.5-2.7 eV defined probably by Mg or Zn impurity. The CL - spectra of these specimens were rather homogeneous. But the areas arounded the cracks emit a light shifted to yellow part of CL-spectrum (Fig.2.1).

Other samples grown in a more pure media show very weak violet or yellow emission depending on the growth conditions, structural and morphological quality of the epilayers. Some samples of this group have very low intensity of emission for visual interval of wavelengths. Typical low-temperature (T=2 K) luminescence spectrum of such GaN sample is presented in the Fig. 2.2. This spectrum has strong, sharp bound exiton line at 3.47 eV.

In Fig.2.3 we can compare the room temperature photoluminescence of various initially undoped GaN samples. For the most part of samples of this group the donor bound exiton recombination at 3.47 eV is more weak. But we see wide band yellow luminescence at 2.2-2.5 eV. Both bands of luminescence are observed also at

low temperatures. The ratio of intensities of exiton to yellow bands depends highly on growth condition (growth temperature, inward flux of ammonia) and can be taken as a measure of the quality of the samples. In the best samples the intensity ratio was 30:1 and the donor bound exiton had a line width of 4 meV.

Using SEM:CL method we found that the samples of initially undoped GaN epilayers demonstrates a spatial inhomogeneous luminescence in the energy interval 2.2 - 2.7 eV.

It was shown that typical luminescence inhomogeneities were recognized on the surface and in the cross section of epilayers. Under high magnification we measure in large quantities of separate bright green spots stand out sharply against the weak luminescened epilayer (Fig. 2. 4). We can also observe local bright yellow or blue spots and strips. Usually we observe areas with bright luminescence near morphological defects of the surface.

The cross section surface of GaN / SiC is demonstrated by Fig. 2.5 (substrate is located at the left-dark area). GaN-layer has a set of light stripes in parallel to the substrate with different luminescence spectra and intensity. As a rule the layer attached to the substrate surface emits in the blue which transforms to a yellow stripe with decrease of intensity. Part of the GaN layers emited very weak CL. Sometimes a blue needlelike formation crossed the GaN epilayer in the growth direction. As a result we are able to see the blue spots on surface.

Studies of GaN layers have shown that real space CL inhomogeneities can not be explained only taking into account the impurities as the epilayers are inhomogeneous, with different levels of impurities, different density of dislocations (across the bulk), and stoichiometry variations. We observed a distribution of defects for specimens grown at uniform impurity composition in external phase. We did not measure an effect of crystallographic orientation dependence on the CL spectrum. However, the CL spectrum of shaped crystals did not depend on orientation and changed during the growth process only. Therefore, we believe that the variation in CL spectra mainly depends on local stoichiometry deviation. The latter is a very complicated function of temperature, rate of ammonia flow, etc. One of possible reason of the yellow band existence in CL it is attributed to defects including Ga-vacancies [5,15]. Different impurity vacancy associations are responsible for different CL-bands [1]. Another factor which modifies the CL spectrum of GaN is a biaxial strain arising from substrate layer lattice mismatch [3].

2.4. Conclusion

Luminescence properties of GaN epilayers grown by sublimation sandwich-method on the SiC and sapphire substrates have been studied. The spatial inhomogeneity luminescence with different emission spectrum (from yellow to blue

and violet) was observed in initially undoped epilayers both over the surface and cross-sections. It is noted the correlation between inhomogeneity of CL emission and morphological and structure defects of epilayers. It is suggested that local stoichiometric variations are responsible for inhomogeneity of luminescence. Interface layer between SiC-substrate and GaN- epitaxial layer with blue emission was discovered.

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3. Electron paramagnetic resonance of impurities.
Identification of iron transition group trace impurities in GaN bulk crystals by electron paramagnetic resonance.

3.1 Introduction

GaN is considered to be one of the most promising semiconductor materials for the construction of short-wavelength emitting devices, such as blue diodes and lasers [1]. In spite of impressive technological achievements of the last few years, there are still substantial gaps in our knowledge of the basic physical properties of GaN. One of them concerns the identification of transition metal impurities in GaN. The presence of these impurities in semiconductors influences the materials' characteristics and device performance. An important question concerns the future of transition-metal impurities as compensators in order to obtain semi-isolating substrates.

The EPR proved to be a powerful method for the identification of transition metal impurities in semiconductors. By now only Fe^{3+} ions were investigated in GaN using EPR [2,3]. The sublimation sandwich-method was used for growing GaN crystals as thick as 0.1 mm [4,5]. It was reported [6,7], that these crystals have good characteristics, no worse than in thin GaN layers grown by other techniques. These crystals have shown at least three zero-phonon lines of photoluminescence in infrared spectrum range: 1.3 eV, 1.19 eV, 1.047 eV [6,7]. It was supposed, that these lines belong to transitions within 3d levels of trace impurities of transition metal ions. The investigations of optically detected magnetic resonance have shown the correspondence between the EPR spectra, attributed to Fe^{3+}, and 1.3 eV luminescence line. The nature of other lines was widely discussed. The experimental results on the 1.047 eV emission [8] fit to a $^4T_2(F)$-$^4A_2(F)$ internal electronic transition of a transition metal with a $3d^7$ electronic configuration. It was suggested [9] that the best candidate was Co^{2+}, but the author could not completely exclude the Ni^{3+}. Thus, only correlation with the EPR seems can clarify this problem. It should be noted that the emission at 1.047 eV has not been observed as natural contaminant in GaN samples grown by metal organic vapor phase epitaxy and vapor phase epitaxy.

3.2. Experimental and discussion

We report here new EPR results for Mn^{2+} and Ni^{3+} in GaN grown by the sublimation sandwich method. Preliminary reports on Mn^{2+} in GaN have been published elsewhere [9].

In this work we investigated GaN crystals grown on 6H-SiC substrates by the sublimation sandwich method [4,5]. The thickness of GaN epitaxial layers was 0.1-0.2 mm and we can say with reasonable confidence that GaN was a bulk material in

our experiments. Epitaxial layers on substrates and free-standing layers were used. No intentional doping of samples was performed. The samples were oriented for rotation in the {1 1 $\bar{2}$ 0} plane. The EPR spectra were studied on a conventional X-band (9.25 GHz) EPR spectrometer in the temperature range 4 - 150 K.

Fig. 3.1 shows a part of the EPR spectrum of a GaN epitaxial layer on a 6H-SiC substrate, recorded at T=4 K for several angles (θ) between the applied magnetic field and the hexagonal axis (*c*-axis) of the sample (rotation in the {1 1 $\bar{2}$ 0} plane). In Fig. 3.1 a set of six equally intense lines can be seen on both sides of the central line. The strong signal near 3300 G contains, except the central fine-structure line of Fe^{3+}, a signal from the nitrogen donor impurity in the 6H-SiC substrate. The latter was nearly suppressed upon removing the substrate. In the orientations $B \| c$ and $B \perp c$ these lines are marked by a set of vertical lines. The separations between the lines are about 70 G. We could observe other four groups with smaller intensities on both sides of central one, which proves that this spectrum belongs to an ion with electron spin S=5/2. All the groups have the same hf structure as the central one. Among the transition metal elements only manganese has a 100% abundant isotope with nuclear spin I=5/2 and the observed splitting corresponds to that of Mn^{2+} in $3d^5$ ($^6S_{5/2}$) state. The group in Fig. 1 belongs to the Mn^{2+} central fine structure transition
($M_S = 1/2 \leftrightarrow M_S = -1/2$), split by the hf interaction with nuclear spin I=5/2.

An investigation of the angular dependence of the spectrum of Mn^{2+} allowed us to find the best-fit parameters for spin Hamiltonian. The results are listed in Table 1 (the small parameters a-$F \cong 4 \cdot 10^{-4} cm^{-1}$ and $a \cong 5 \cdot 10^{-4} cm^{-1}$ are not pointed out in the table). The measured and calculated angular dependencies of fine-structure line positions of Mn^{2+} ions obtained at 9.25 GHz are plotted as open circles and dashed lines, respectively, in Fig. 3.2. The fine-structure positions have been estimated as the center of gravity of the measured hf structure transitions. The solid circles and solid lines represent the measured and calculated hf structure positions, which are plotted only for central transition ($M_S = 1/2 \leftrightarrow M_S = -1/2$).

In Fig. 1 for the orientations $\theta = 10^0$ and 15^0 one can see intense broad EPR line, attributed [2] to one of the fine-structure transitions of Fe^{3+} with electron spin S=5/2. With increasing temperature EPR signals of Mn^{2+} and Fe^{3+} decrease in a similar manner. Fe^{3+} and Mn^{2+} EPR signals are detectable up to ~100 K.

An intense anisotropic EPR line was observed in some GaN crystals. Fig. 3.3 shows an angular dependence of these line in GaN crystal at the X-band. The magnetic field applied was rotated in the {1 1 $\bar{2}$ 0} plane. This EPR spectrum has the characteristic anisotropy of an S=3/2 system in a strong axial crystalline field and positive g shift which is consistent with the electron configuration d^7 . The EPR

line can be observed up to ~150 K and the linewidth is very sensitive to the orientation of the crystal in magnetic field. The intensities of the EPR signals for $\theta \neq 0$ at 77 K are lower and depend more on the angle between magnetic field and *c*-axis then those at 4 K. Therefore it has not been possible to detect the signals at all angles at 77 K.

We attribute this spectrum to the trace impurity of nickel in the charge state Ni^{3+}. Isolated substitutional Ni^{3+} ion has a $3d^7$ electronic configuration.

In Ref.[2], an analogy was revealed between the parameters of Fe^{3+} ions in GaN and ZnO crystals. It was taken into account that both materials have the same hexagonal wurzite structure and close by similar physical parameters. We will follow this analogy in the case of Mn^{2+} and Ni^{3+} and the Table 1 lists corresponding values previously obtained for ZnO: Mn^{2+} [13] and ZnO: Ni^{3+} [12] (the parameters for Mn^{2+} in ZnO, a-F=$5.2 \cdot 10^{-4}$cm^{-1} and a=$6.2 \cdot 10^{-4}$cm^{-1}, are not pointed out in the Table 1). As illustrated in Table 1, a good correspondence is observed between the parameters of Fe^{3+}, Mn^{2+} and Ni^{3+} in GaN and ZnO. The small quantitative variation in the EPR parameters seems to reflect the changing degree of covalency. By analogy with Fe^{3+} in GaN we suppose that manganese and nickel occupy gallium sites in the GaN lattice. Since no hf structure for the line which we attributed to Ni^{3+} was observed we could not completely exclude some impurities which are isoelectronic to Ni^{3+} and have small concentration of odd isotopes or a very small value of nuclear magnetic moment, e.g., Fe^{+} or ions with $4d^7$ and $5d^7$ configurations.

According to our investigations we have every reason to think, that zero-phonon luminescence line at 1.047 eV belongs to transition $^4T_2(F)$-$^4A_2(F)$ within 3d levels of Ni^{3+} ion with a $3d^7$ electronic configuration. This luminescence line has been observed only in GaN samples grown by the sandwich technique and seems to correlate with EPR spectra of Ni^{3+}. This assumption is consistent with the experiments of Ref. [8] in which photoluminescence results on the 1.047 eV emission fit to a $^4T_2(F)$-$^4A_2(F)$ internal electronic transition of a transition metal with a $3d^7$ electronic configuration. It should be noted that Fe^{3+} (the same charge state as Ni^{3+}) has the stable configuration in *n*-type GaN material and it's EPR spectra have been observed in the same samples in which the EPR spectra of Ni^{3+} were recorded.

On the basis of the EPR investigations we have estimated the impurity concentrations in several GaN crystals used in our experiments at 10^{17} - 10^{18} cm^{-3} for Fe, and 10^{16} - 10^{17} cm^{-3} for Mn and Ni. We would finally like to comment on possible sources of Fe, Mn and Ni contaminations in GaN crystals grown by the sandwich sublimation technique. Fe and Mn contamination during the growth process may result from container material of the Ga source. Ni contamination may result from SiC substrate which was etched in molten KOH with using of the container from the nickel material.

In addition, the energy level scheme of transition metals in GaN, as inferred from known levels in other III-V compounds via the Langer Heinrich rule, indicates, that the acceptor levels of Mn and Ni are close to mid-gap [14]. Therefore Mn and Ni seem to be more suitable dopants for the creation of semi-insulating GaN substrates as previously discussed Fe and Cr.

In some GaN samples the EPR spectra of shallow donors were detected. Fig. 3.4 shows the EPR spectra of shallow donors (single line at 3400 G). The strong line at 3300 G is due to the nitrogen donors in 6H-SiC-substrate. The g-factors for this line are: $g_{||} = 1.9547$, $g_{\perp} = 1.9520$, which coincide with those reported earlier [15]

3.3. Conclusion

We report on the observation of electron paramagnetic resonance of iron, manganese and nickel trace impurities in bulk GaN crystals grown by the sublimation sandwich method. The resolved hyperfine structure due to interaction with ^{55}Mn (I=5/2) nuclei has been observed in GaN, allowing unambiguous identification of the impurity . Manganese and nickel exist in Mn^{2+} ($3d^5$) and Ni^{3+} ($3d^7$) charge states with electron spin S=5/2 and S=3/2, respectively, and occupy gallium sites in the GaN lattice. For Mn^{2+} we found g=1.999, hyperfine structure constant $A=70\cdot10^{-4}cm^{-1}$ and fine structure parameter $/D/ = 240\cdot10^{-4}cm^{-1}$. The EPR spectrum of Ni^{3+} in GaN had the characteristic anisotropy of an S = 3/2 system in a strong axial crystalline field. The effective g-factor values were found to be $g_{||}' = 2.10$ and $g_{\perp}' \cong 4.20$ for a system with an effective spin $S' = 1/2$. An analogy was revealed between the parameters of Mn^{2+} and Ni^{3+} in GaN and ZnO crystals. The zero-phonon line at 1.047 eV seems to belong to transition $^4T_2(F)$-$^4A_2(F)$ within 3d levels of Ni^{3+} ion with a $3d^7$ electronic configuration.

3.4. References

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Table captions

Table 1. The parameters of the spin Hamiltonian of Eq. (1) for Fe^{3+} and Mn^{2+} ions and of the spin Hamiltonian of Eq. (2,3) for Ni^{3+} ions in GaN and ZnO.

	GaN					ZnO				
	$g_{\|\|}$	$g_{\perp}$	$\|D\|$ $10^{-4}cm^{-1}$	A $10^{-4}cm^{-1}$	Ref.	$g_{\|\|}$	$g_{\perp}$	D $10^{-4}cm^{-1}$	A $10^{-4}cm^{-1}$	Ref.
Fe^{3+} ($3d^5$)	1.990 1.995	1.997 1.995	713 715		[2] this work	2.006	2.006	-595		[2]
Mn^{2+} ($3d^5$)	1.999	1.999	240	70	this work	2.001	2.001	-236	74.1	[13]
Ni^{3+} ($3d^7$)	2.10 2.10	≅4.2 ≅2.1	≥$1.5\cdot10^4$		this work S′=1/2 S=3/2	2.142 2.142	4.318 ≅2.16	+$2\cdot10^4$		[12] S′=1/2 S=3/2

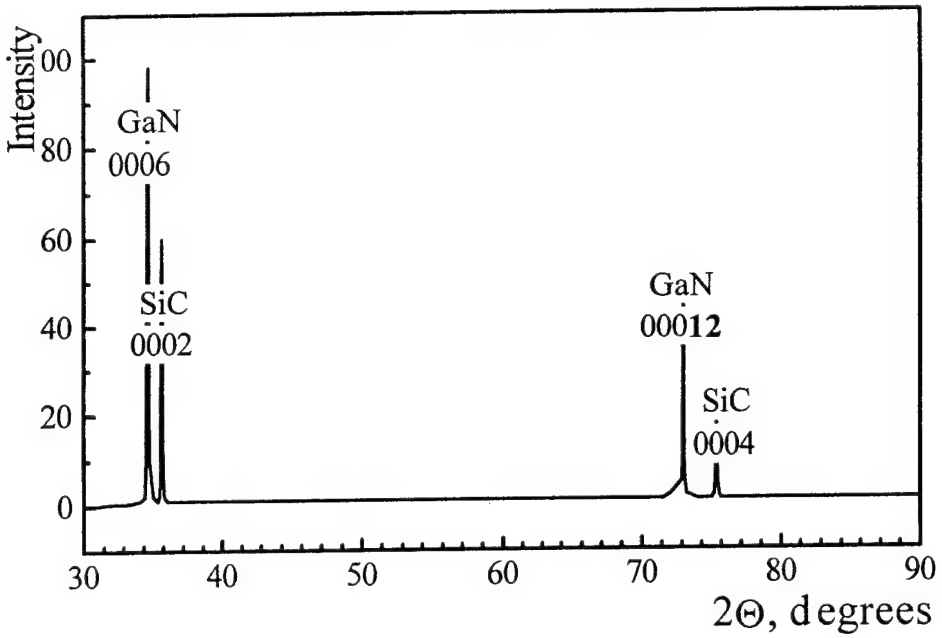

Fig.1.1. X-ray diffraction pattern for GaN layers deposited on 6H-SiC (0001) substrate by SSM. (0002) & (0004) peaks from SiC and (0006) &(00012) from GaN observed in Θ-2Θ scan.

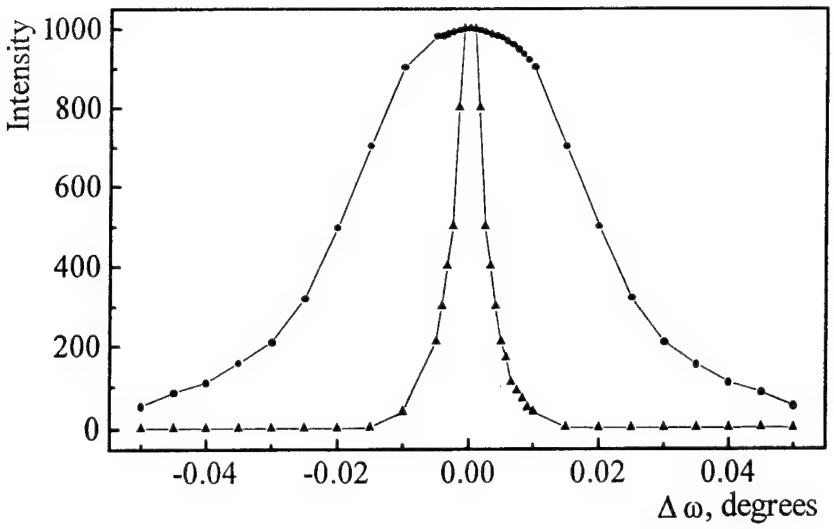

Fig.1.2. Comparison the shape of XRD
⊗ - (0002) SiC substrate and for
∇ - (0006) GaN epilayer by ω-scan.

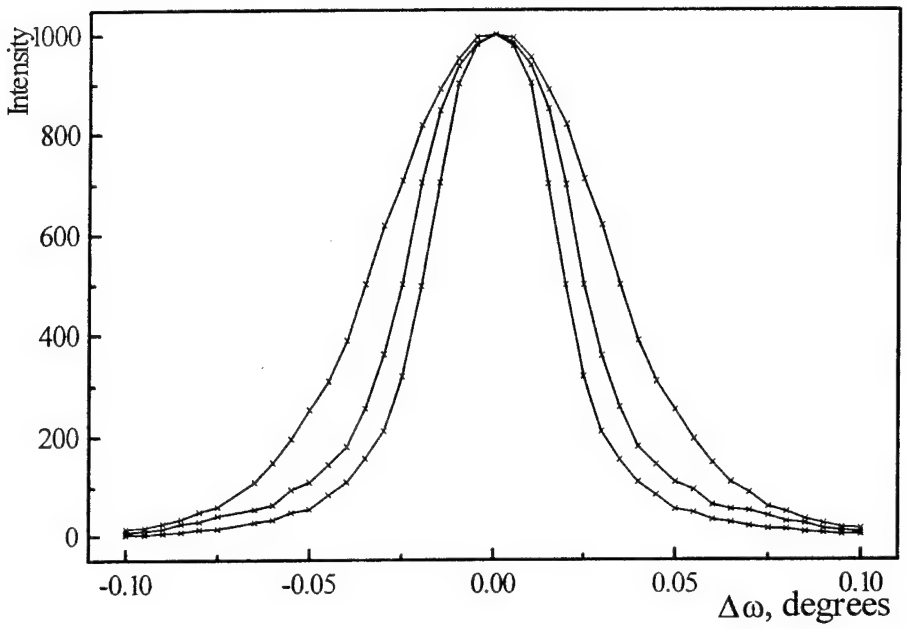

Fig.1.3. Typical rocking curve from different heterostructures GaN/SiC.

a). GaN/SiC No 1364. FWHM = 150''

b). GaN/SiC No 1520 FWHM = 180''

c). GaN/SiC No 1645 FWHM = 350''

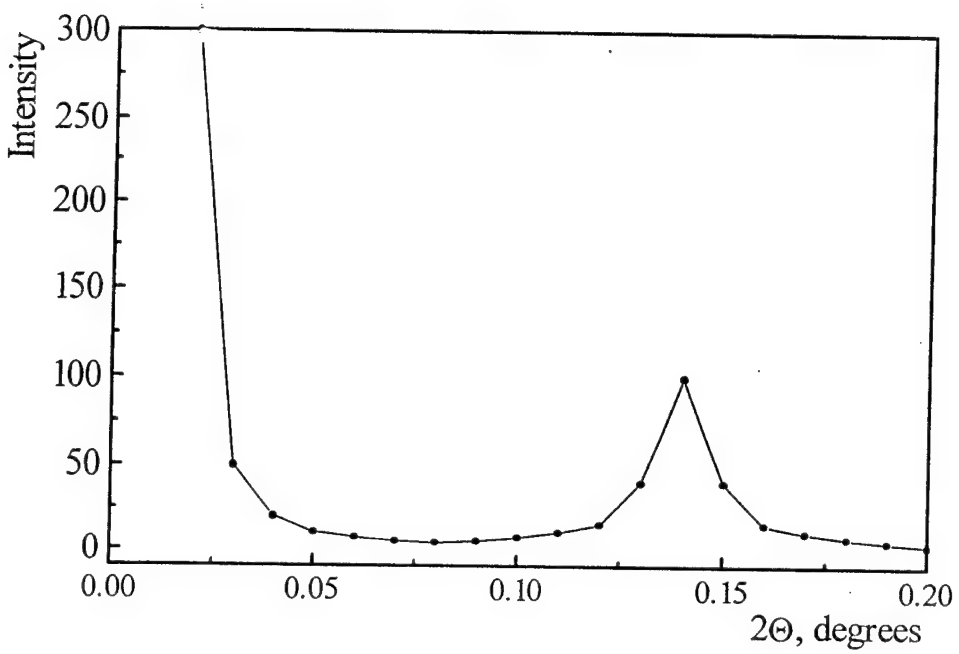

Fig.1.4 . X-ray diffraction profiles for S AS of GaN film deposited on SiC substrate. It is seen the peak near 0.135°-0.15° This value corresponds (using Wulf-Bragg dependence: $2ds\sin\Theta=n\lambda$) 65nm-50nm

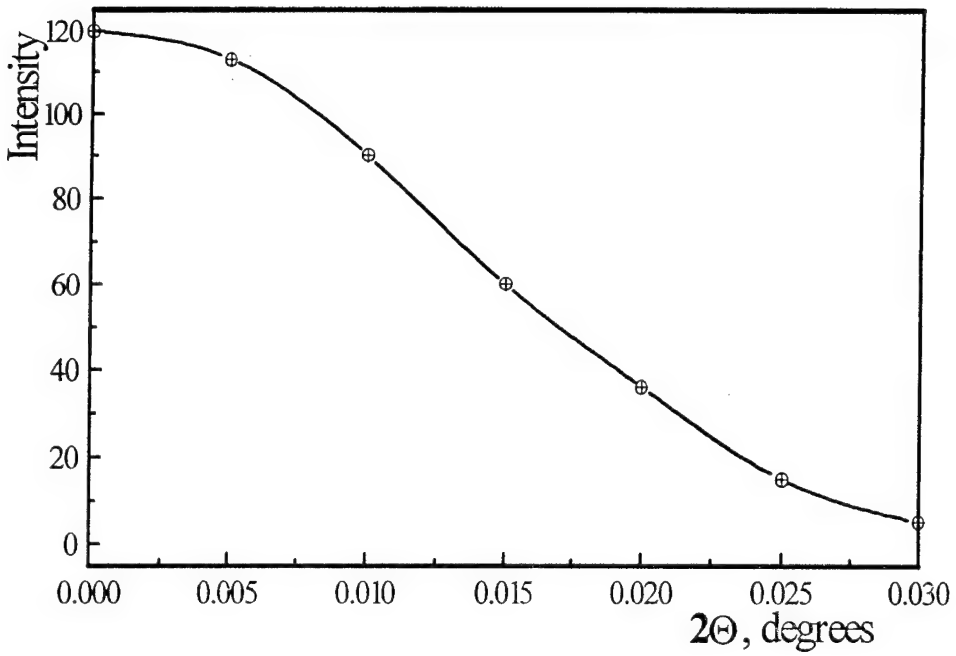

Fig. 1.5. Dependence intensity of S AS versus angle for GaN film deposited on Al_2O_3 substrate. Smooth curve of broadening incident beam. This corresponds to gas-like allocation of domains.

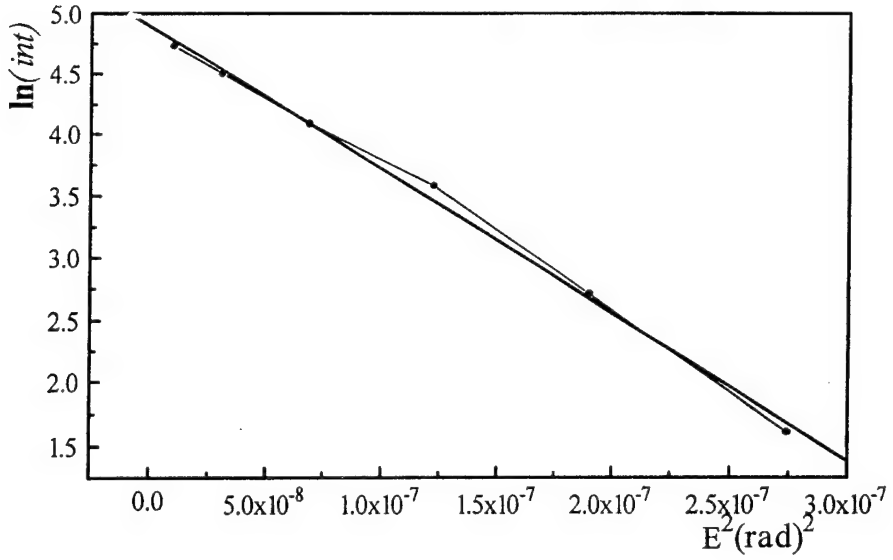

Fig.1.6. Logarithmic dependence intensity of S AS versus scattering square angle for GaN film deposited on Al_2O_3 substrate. Linear approximation of this dependence shows coefficient for measurement of distances between clasters in GaN film.
Linear appreoximation: $Y=B*X+X_o$; Distance $R_o \sim \sqrt{B}$.
In this case B=1.17E007 R_o =220nm.

Fig.2.1.Real CCL+BSE-SEM image of the surface of the GaN epilayers grown on SiC-substrates.
Effective blue luminescence and yellow stripes around cracks.

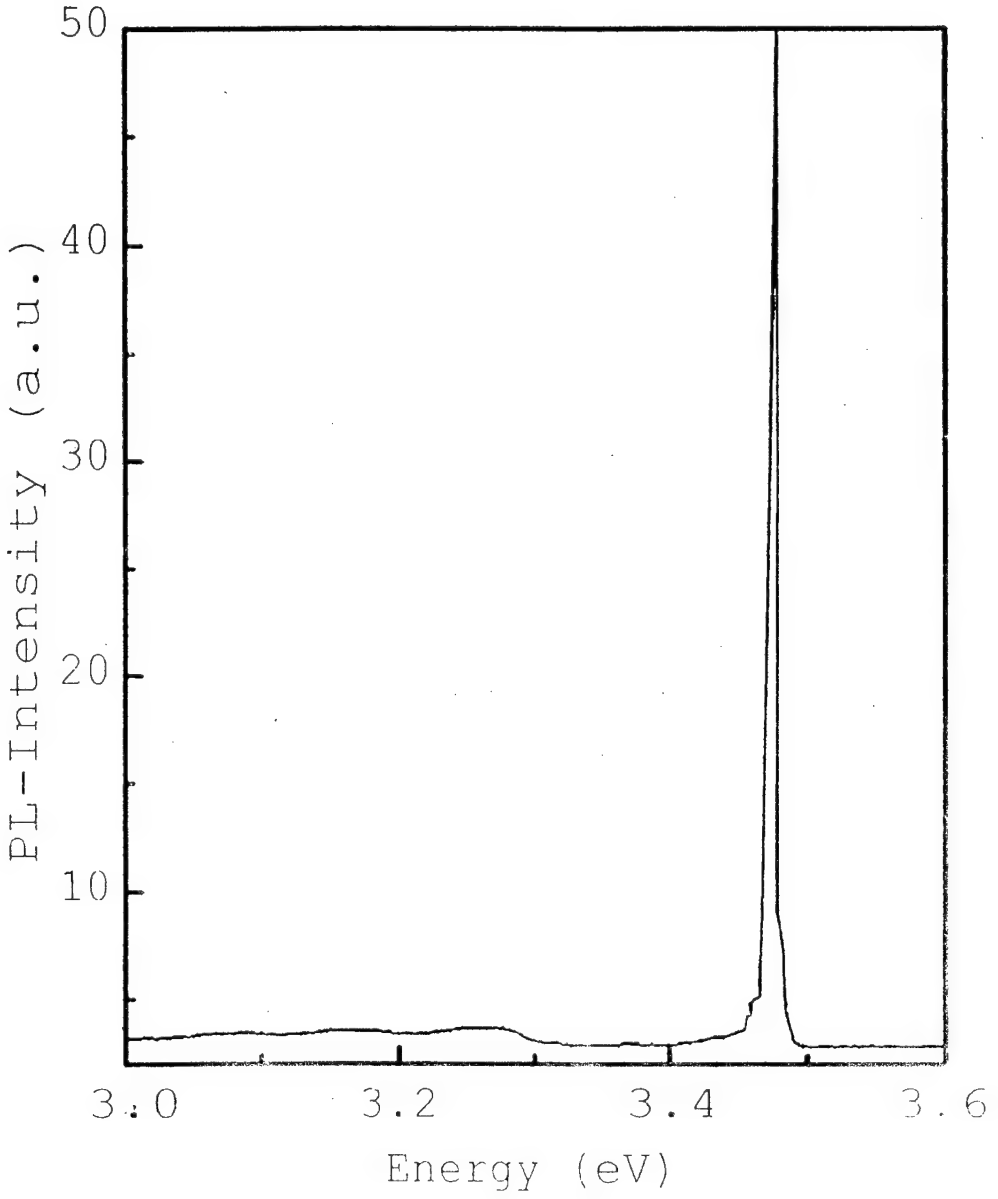

Fig. 2.2. Luminescence of high quality GaN epilayer at low temperature (2 K).

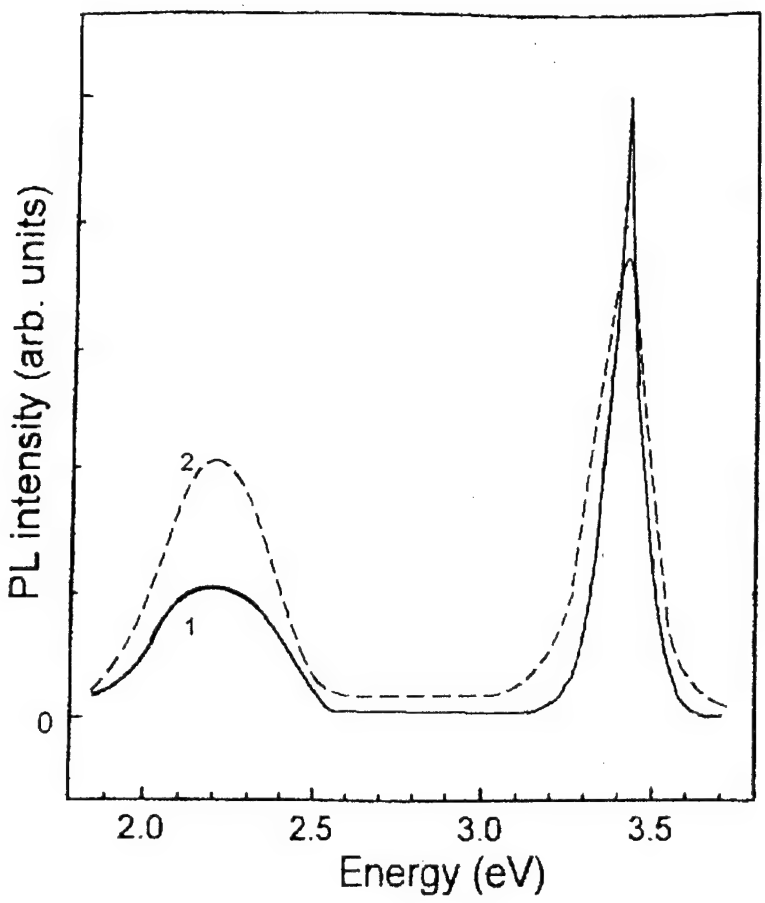

Fig. 2. 3 Photoluminescence spectra at room temperature for two GaN epilayers grown on SiC substrates at different temperatures ^{O}C; 1140 - solid curve; 1210 - dotted curve.

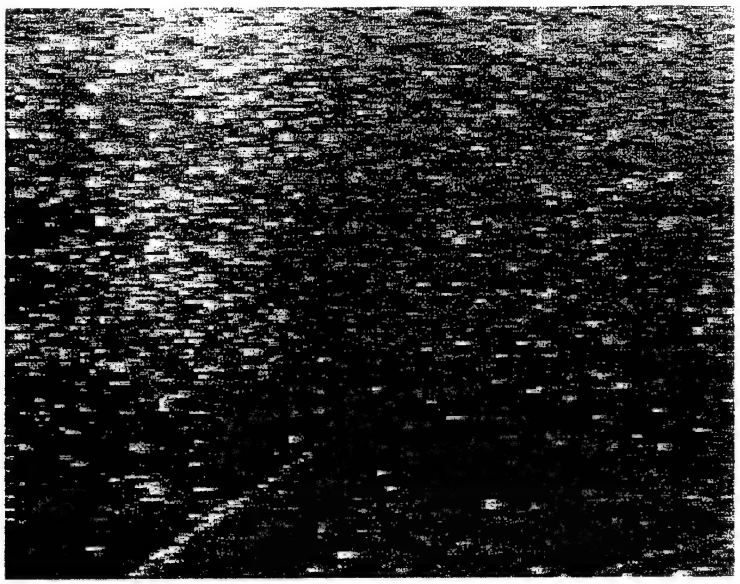

Fig2.4. Real CCL-SEM image of the surface of the initial undoped GaN epilayers grown on SiC substrate. Separate bright greenish spots are seen.

Fig.2.5 Real CCL - SEM image of cross-section of the GaN epilayer grown on SiC substrates (0.3 mm thickness). Blue stripe is interface layer between substrate (at the left) and grown GaN-epilayers (at the right).

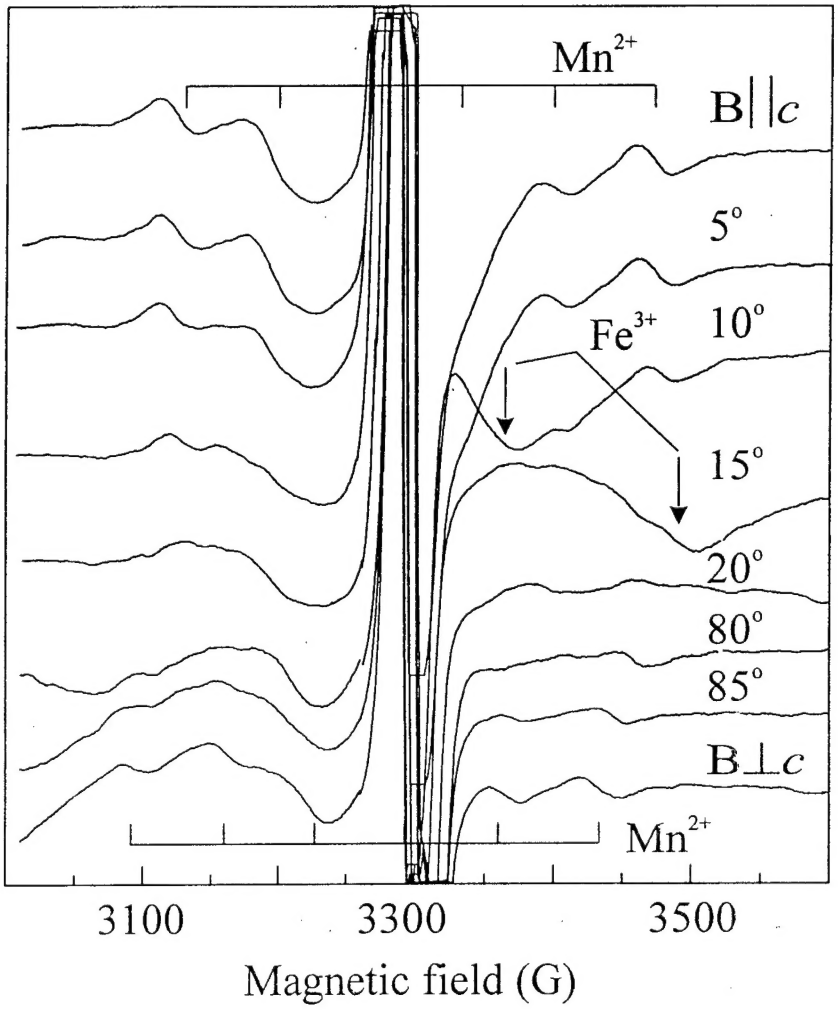

Fig.3.1. EPR spectrum of Mn^{2+} ions in GaN in some orientations of crystal under rotation in {110} plane. In orientations B// *c* and B⊥ *c* the positions of hf structure transition of Mn^{2+} (M_S=1/2 M_S=-1/2) are indicated. The arrows indicate positions of Fe^{3+} EPR signal.

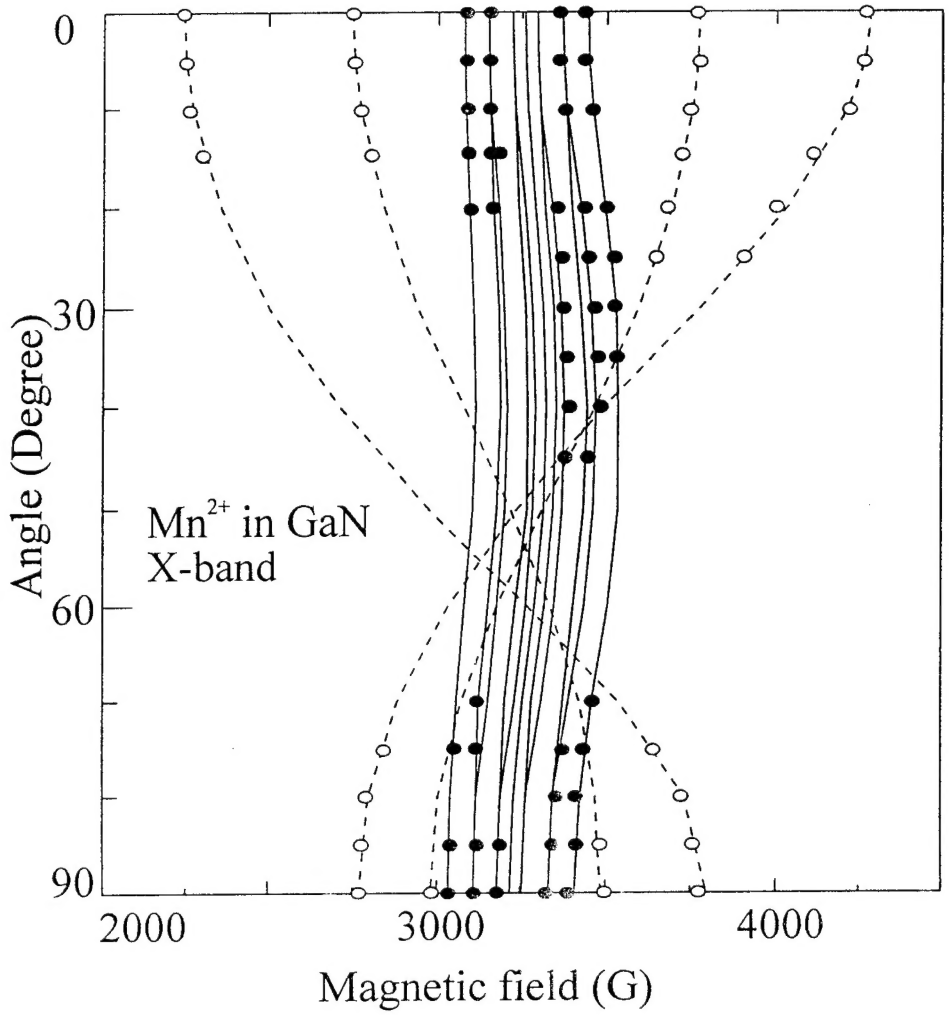

Fig.3.2. The measured (open circles) and calculated (dashed lines) angular dependencies of fine-structure line positions of Mn^{2+} ions in GaN obtained at 9.25 GHz. The solid circles and solid lines represent the measured and calculated hf structure positions, respectively, which are plotted only for central transition (M_S= 1/2 M_S= -1/2).

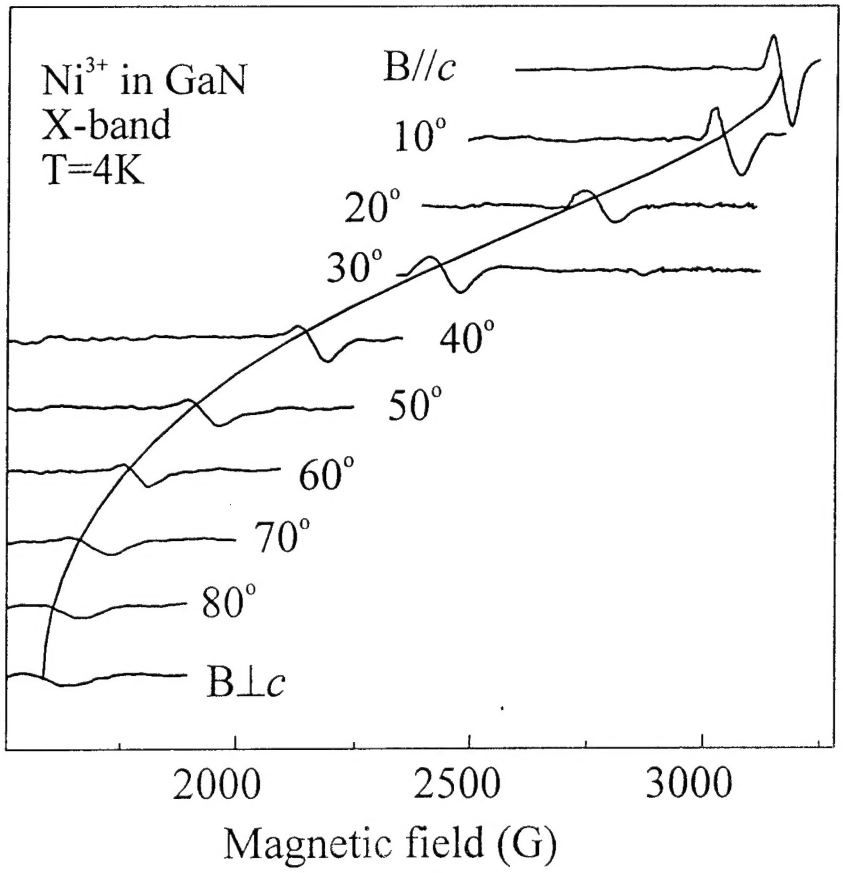

Fig.3.3. Angular dependence of Ni^{3+} EPR line for rotation of the GaN crystal in {110} plane. Solid line have been calculated using spin Hamiltonian parameters , listed in the text

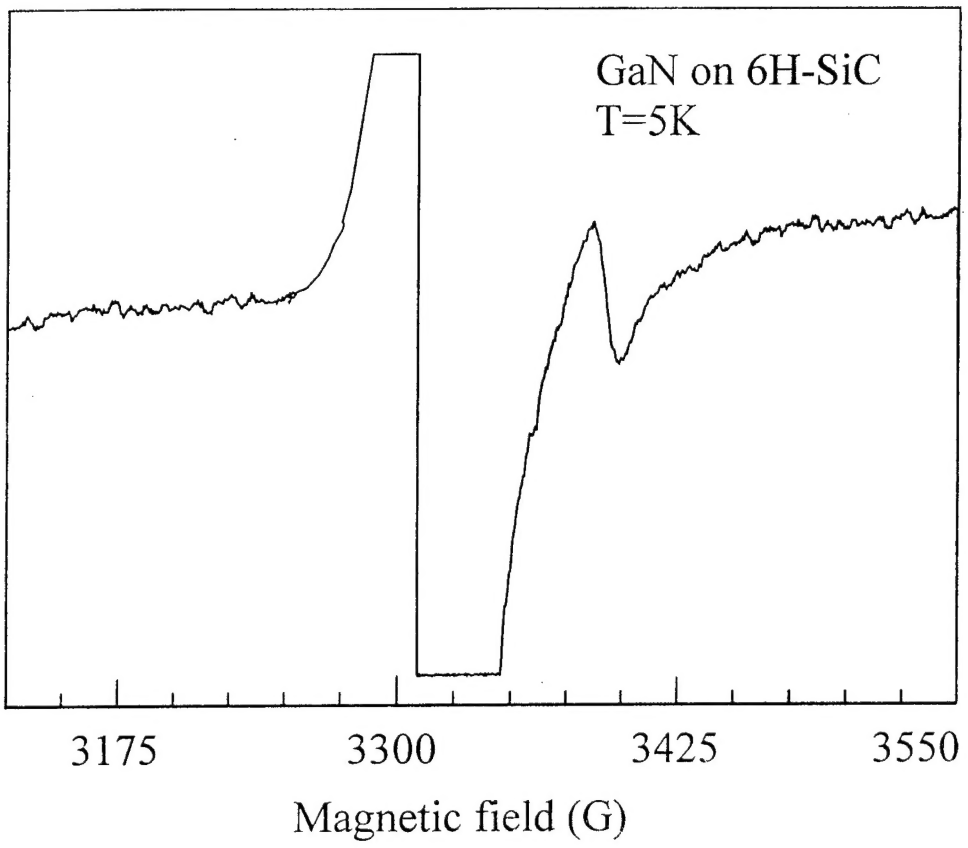

Fig.3.4. EPR spectrum of shallow donors in GaN crystal, grown by the sublimation sandwich-method (near 3400G). The strong line near 3300G corresponds to the nitrogen donors in the 6H-SiC substrate.